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Spin Density Distribution in Radical Anions of Unsubstituted & Methyl Substituted Aza-aromatics

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The spin density distribution in the radical anions of unsubstituted and methyl substituted aza-aromatics have been evaluated using UHF method. The nitrogen splittings (a_N) have been calculated using the relation of Karplus and Fraenkal. The values of Q^N_N and Q^N_{CN} are found to be 21·23 and 0·58 gauss respectively. The small value of Q^N_{CN} further indicates that a simple one parameter relation may be quite adequate for predicting nitrogen splittings in aza-aromatic radical anions.

ELECTRON spin resonance data for a large number of substituted and unsubstituted aza-aromatic radical anions are available in the literature[1-13]. The observed splitting constants can be explained in terms of spin denity distribution in these systems using various relations between spin density and splitting constants[14-21]. Many attempts have been made to study the relation between nitrogen splitting and the spin density distribution in aza-aromatic radical anions. Most of these studies[1-7,18,21,22] have mainly made use of HMO and McLachlan type of calculations. For some of the systems reported here more sophisticated π-electron calculations, namely configuration interaction (CI) calculations[24] and restricted Hartree-Fock (RHF) calculations[25] and unrestricted Hartree-Fock (UHF) calculations[26-28] have also been done.

However, in none of these studies the applicability of Karplus-Fraenkel relation[19] for ^{14}N splitting (a_N) has been adequately tested for a large number of substituted and unsubstituted aza-aromatic radical anions using a π-electron theory in which the arbitrary choice of parameters has been reduced to the minimum. The results of such a study are being reported[23] in this paper.

Method of Calculations

The unrestricted Hartree-Fock (UHF) method of Snyder and Amos[28] has been employed in the present study. The spin densities and charge densities were obtained after annihilation of the quartet spin component from the UHF wave functions. All the molecules were assumed to be planar and C-C and C-N distances within the ring were taken equal to 1·40 Å and 1·34 Å respectively. The bond joining the two rings (in aza-substituted triphenyl derivatives) was taken equal to 1·48 Å.

Valence state ionization potentials (I_k) and electron affinities (E_k) of carbon and nitrogen $2p_\pi$ orbitals needed for the computation of one-centre two-electron repulsion integrals were taken from the literature[29]. Two-centre two-electron repulsion integrals were obtained using Ohno's relation[30]. Resonance integrals (β_{rs}) for various bonds were obtained using Linderberg's relation[31]. According to this relation the gradient of the overlap is related to the resonance integral by the relation

$$\beta_{rs} = \frac{1}{R_{rs}} \frac{dS_{rs}}{dR_{rs}} \qquad ...(1)$$

Effective nuclear charges for various atoms were taken from the work of Mulliken *et al.*[32]. Approximate starting density matrices needed for SCF-iteration procedure were obtained from simple HMO wave functions and the various heteroatom parameters needed for the HMO calculations were taken from Streitwieser[33]. Topologies of the systems studied are given in Fig. 1. All calculations reported in this paper were done on IBM 360/44.

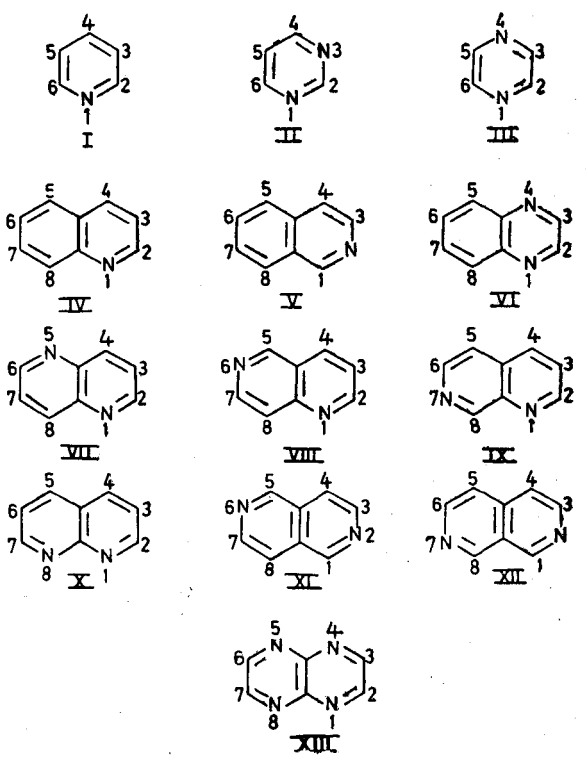

Fig. 1

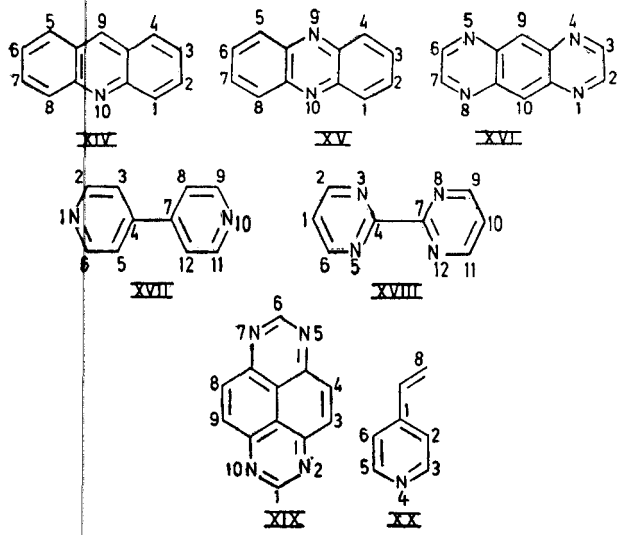

Fig. 2

Results and Discussion

In a situation where nitrogen is bonded to two carbon atoms (C and C′) the ^{14}N splitting is bilinear in ρ_N (the spin density on nitrogen) and $\rho_C+\rho_{C'}$ (the sum of the spin densities on C and C′) can be written as

$$a_N = (S^N+2Q^N_{NC})\rho_N+Q^N_{CN}(\rho_C+\rho_{C'}) \quad \ldots(2)$$

where S^N and Q^N_{NC} describe the contribution from spin density on nitrogen under consideration and Q^N_{CN} takes into account the effect of spin density on adjacent carbon atoms. The relation (2) can be written as

$$a_N = Q^N_N\rho_N+Q^N_{CN}(\rho_C+\rho_{C'}) \quad \ldots(3)$$

where

$$Q^N_N = (S^N+2Q^N_{NC}) \quad \ldots(4)$$

Many attempts have been made earlier to obtain Q^N_N and Q^N_{CN} and the results of these studies have been summarized more recently by Zeiss *et al.*[34]. The nitrogen splitting (a_N) calculated from Karplus and Fraenkel relation (3) shows good agreement with experimental values. In the present work the following relation has been used:

$$a_N = Q^N_N\rho_N+Q^N_{CN}(\rho_C+\rho_{C'})+K \quad \ldots(5)$$

where K is a constant.

The results of the present calculations along with those of Zeiss *et al.*[34] are given in Table 1 along with the experimental nitrogen splittings. The best values of Q^N_N and Q^N_{CN} determined by the least squares fit, using UHFAA spin densities and the experimental splitting constants are 21·23 and 0·58 gauss respectively. It is clear from Table 1 that the standard derivation is lowest in the present study. A calculated small value (0·58) for Q^N_{CN} also explains why a simple one-parameter relation

$$a_N = Q\rho_N \quad \ldots(6)$$

explains[18,26] the nitrogen splitting in a satisfactory manner for most of the aza-aromatics systems. A least squares fit analysis of Eq. (6) gives a value of 21·8 gauss for the proportionality constant Q.

Table 1 — Nitrogen Hyperfine Splittings in Anions[a]

Method	No. of points	Q^N_N	Q^N_{CN}	K	St. dev.[b] (1)	St. dev.[b] (2)
RHF	13	16·2	−2·25	2·04	1·01	1·31
RHF-CI	7	18·7	2·63	0·07	0·56	0·56
UHF	13	17·2	2·79	−0·13	0·71	0·71
UHF-PR	13	17·7	1·97	0·64	0·75	0·79
Present work	39	19·85	−0·37	0·46	0·35	0·39

(a) See reference 34.

(b) (1) With respect to the line determined by the listed values of appropriate constants. (2) With respect to a line required to pass through the origin.

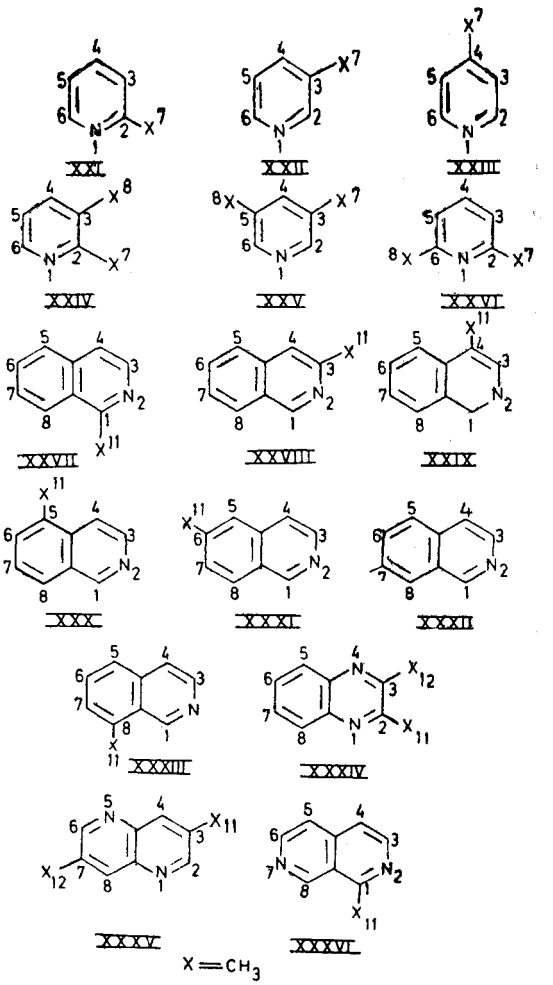

Fig. 3

The nitrogen splitting (a_N) calculated from relation (6) using the above value of Q are given in Table 2. The results are in good agreement with experiment. From the present study it appears that a simple one-parameter relation may be quite adequate for predicting nitrogen splittings in aza-aromatic radical anions if Q is given the value 21·8 gauss.

The proton splittings were calculated using the McConnell relation and Colpa-Bolton relation. The results of such a study are given in Table 3

TABLE 2 — NITROGEN HYPERFINE SPLITTINGS IN ANIONS LEAST ρ_N

System	ρ_N	a_N		System	ρ_N	a_N	
		Calc.	Obs.			Calc.	Obs.
I	0·279	6·09	6 28	XIX	0·099	2·16	2·57
II	0·135	2·95	3·26	XX	0·211	4·61	3·95
III	0·326	7·12	7·19	XXI	0·254	5·54	5·64
IV	0·162	3·54	3·83	XXII	0·288	6·29	6·34
V	0·090	1·96	2·28	XXIII	0·284	6·20	5·67
VI	0·257	5·61	5·70	XXIV	0·295	6·44	5·78
VII	0·152	3·32	3·37	XXV	0·306	6·68	6·40
VIII	0·121	2·64	3·04	XXVI	0·237	5·17	4·86
	0·036	0·79	2·03				
IX	0·200	4·37	4·53	XXVII	0·060	1·31	1·72
	0·083	1·81	1·80				
X	0·098	2·14	2·39	XXVIII	0·095	2·07	2·48
XI	0·133	2·90	3·42	XXIX	0·095	2·07	2·40
XII	0·035	0·76	0·36	XXX	0·104	2·27	2·17
XIII	0·175	3·82	3·40	XXXI	0·079	1·72	1·92
XIV	0·257	5·61	5·15	XXXII	0·097	2·12	2·54
XV	0·135	2·95	3·48	XXXIII	0·093	2·03	2·61
XVI	0·120	2·62	2·42	XXXIV	0·240	5·24	5·21
XVII	0·139	3·03	3·59	XXXV	0·155	3·38	3·25
XVIII	0·077	1·68	1·41	XXXVI	0·017	0·37	0·12
					0·047	0·89	0·84

Standard deviation = 0·393.

TABLE 3 — SPIN DENSITIES (ρ_i), ELECTRON DENSITIES (q_i) AND RING PROTON SPLITTING CONSTANTS IN THE RADICAL ANIONS OF SOME AZA-AROMATICS[a]

System/ Position[b]	$<S^2>_{(ba)}$	$<S^2>_{aa}$	ρ_i	q_i	a_i^M	a_i^{CB}	$[a_i]_{obs.(C)}$
			AZA-AROMATICS, I				
2			0·137	0·978	−3·70	−3·74	3·55
3	0·794	0·751	0·010	1·129	−0·27	−0·24	0·82
4			0·428	1·247	−11·56	−10·21	9·70
			II				
2			−0·013	0·711	0·35	0·41	0·72
4	0·814	0·750	0·409	1·093	−11·04	−10·56	9·78
5			−0·074	1·084	2·00	1·93	1·31
			III				
2	0·772	0·750	0·087	1·017	−2·35	−2·33	2·63
			IV				
2			0·128	0·933	−3·46	−3·57	4·40
3			0·028	1·142	−0·76	−0·71	0·86
4			0·337	1·156	−9·10	−8·44	8·44
5	0·816	0·753	0·189	1·137	−5·10	−4·76	4·06
6			0·012	1·105	−0·32	−0·32	0·73
7			0·064	1·071	−1·73	−1·68	2·40
8			0·123	1·170	−3·32	−3·05	2·73
			V				
1			0·312	1·036	−8·42	−8·27	7·16
3			−0·015	0·872	0·41	0·44	0·11
4			0·134	1·250	−3·62	−3·19	4·20
5	0·817	0·753	0·136	1·190	−3·67	−3·35	4·20
6			0·119	1·100	−3·21	−3·06	2·53
7			−0·012	1·070	0·33	0·32	0·11
8			0·261	1·172	−7·05	−5·47	5·16
			VI				
2			0·116	0·987	−3·13	−3·15	3·33
5	0·798	0·752	0·114	1·122	−3·08	−2·89	2·38
6			0·030	1·088	−0·81	−0·77	1·45

TABLE 3 — SPIN DENSITIES (ρ_i), ELECTRON DENSITIES (q_i) AND RING PROTON SPLITTING CONSTANTS IN THE RADICAL ANIONS OF SOME AZA-AROMATICS[a] — *contd*

Position[b]	$<S^2>_{ba}$	$<S^2>_{aa}$	ρ_i	q_i	a_i^M	a_i^{CB}	$[a_i]_{obs.}$[c]
			VII				
2			0·084	0·941	−2·27	−2·35	3·01
3	0·815	0·753	0·047	1·130	−1·27	−1·20	1·72
4			0·240	1·130	−6·48	−6·09	5·80
			VIII				
2			0·179	0·944	−4·83	−4·76	5·45
3			−0·008	1·129	0·22	0·21	0·10
4	0·823	0·753	0·377	1·145	−10·18	−9·47	8·11
5			0·254	0·983	−6·86	−6·92	5·54
7			0·010	0·877	−0·27	−0·29	1·01
8			0·078	1·226	−2·11	−1·89	1·01
			IX				
2			0·074	0·924	−2·00	−2·07	2·93
3			0·072	1·143	−1·94	−1·80	2·09
4	0·823	0·753	0·267	1·155	−7·21	−6·69	6·15
5			0·131	1·200	−3·54	−3·19	3·60
6			−0·026	0·909	0·70	0·75	0·25
8			0·217	1·003	−5·86	−5·86	4·99
			X				
2			0·129	0·916	−3·48	−3·63	4·38
3	0·838	0·755	0·005	1·157	−0·14	−0·12	0·50
4			0·299	1·107	−8·07	−7·65	6·69
			XI				
1			0·228	1·020	−6·16	−6·10	6·02
3	0·818	0·753	−0·038	0·885	1·03	1·09	0·45
4			0·162	1·216	−4·37	−3·93	4·39
			XII				
1			0·362	1·040	−9·77	−9·59	7·43
3	0·812	0·752	0·027	0·875	−0·73	−0·77	2·06
4			0·101	1·258	−2·73	−2·40	3·68
			XIII				
2	0·829	0·753	0·094	0·980	−2·54	−2·56	3·41
			XIV				
1			0·056	1·114	−1·51	−1·42	−1·60
2			0·055	1·048	−1·49	−1·46	2·19
3	0·831	0·755	0·002	1·108	−0·05	−0·05	0·81
4			0·127	1·065	−3·43	−3·33	2·73
9			0·403	1·136	−10·88	−10·17	7·74
			XV				
1	0·812	0·753	0·082	1·080	−2·21	−2·13	1·80
2			0·031	1·075	−0·84	−0·80	1·54
			XVI				
2	0·884	0·760	0·079	0·961	−2·13	−2·18	2·73
9			0·171	1·189	−4·62	−4·22	3·96
			XVII				
2	0·792	0·751	0·016	0·894	−0·43	−0·46	0·44
3			0·079	1·133	−2·13	−2·00	2·37
			XVIII				
1	0·782	0·751	0·102	1·271	−2·75	−2·39	4·98
2			−0·012	0·800	0·32	0·35	0·15

TABLE 3 — SPIN DENSITIES (ρ_i), ELECTRON DENSITIES (q_i) AND RING PROTON SPLITTING CONSTANTS IN THE RADICAL ANIONS OF SOME AZA-AROMATICS[a] — *contd*

Position[b]	$<S^2>_{ba}$	$<S^2>_{aa}$	ρ_i	q_i	a_i^M	a_i^{CB}	$[a_i]_{obs.(C)}$
			XIX				
1	0·811	0·753	−0·023	0·692	0·62	0·72	0·36
3			0·085	1·073	−2·30	−2·29	2·39
			XXI				
3	0·795	0·751	0·051	1·200	−1·38	−1·24	1·56
4			0·436	1·239	−11·77	−10·44	9·53
5			−0·022	1·111	0·59	0·58	<0·10
6			0·194	1·011	−5·24	−5·22	4·39
			XXII				
2	0·794	0·751	0·186	1·043	−5·02	−4·91	4·07
4			0·406	1·266	−10·96	−9·57	9·61
5			0·038	1·148	−1·03	−0·95	1·35
6			0·094	0·963	−2·54	−2·59	2·68
			XXIII				
2	0·814	0·752	0·170	0·975	−4·59	−4·63	3·68
3			−0·019	1·142	0·51	0·48	0·60
			XXIV				
4	0·783	0·750	0·414	1·276	−11·18	−9·73	8·66
5			0·011	1·099	−0·30	−0·28	0·82
6			0·127	1·040	−3·43	−3·38	2·89
			XXV				
2	0·792	0·751	0·140	1·027	−3·78	−3·73	3·18
4			0·387	1·288	−10·45	−9·02	8·85
			XXVI				
3	0·792	0·751	0·012	1·177	−0·32	−0·30	0·71
4			0·460	1·239	−12·42	−11·02	9·29
			XXVII				
3	0·811	0·752	−0·011	0·873	0·30	0·32	0·27
4			0·104	1·263	−2·81	−2·47	3·23
5			0·149	1·208	−4·02	−3·63	3·81
6			0·148	1·109	−4·00	−3·78	3·81
7			−0·022	1·061	0·59	0·58	0·27
8			0·296	1·186	−7·99	−7·28	5·73
			XXVIII				
1	0·817	0·753	0·322	1·030	−8·69	−8·56	7·06
4			0·120	1·284	−3·24	−2·80	2·48
5			0·128	1·193	−3·46	−3·15	4·00
6			0·123	1·099	−3·32	−3·17	4·00
7			−0·017	1·075	0·46	0·44	0·29
8			0·263	1·167	−7·10	−6·54	5·27
			XXIX				
1	0·818	0·753	0·280	1·038	−7·56	−7·42	7·03
3			−0·025	0·910	0·68	0·72	0·35
5			0·153	1·198	−4·13	−3·74	4·70
6			0·120	1·106	−3·24	−3·07	2·69
7			−0·009	1·065	0·24	0·24	0·35
8			0·268	1·184	−7·24	−6·60	5·63
			XXX				
1	0·815	0·753	0·326	1·051	−8·80	−8·60	7·89
3			−0·021	0·872	0·57	0·59	0·20
4			0·147	1·257	−3·97	−3·48	3·95
6			0·105	1·137	−2·84	−2·65	3·95
7			−0·014	1·055	0·38	0·38	0·20
8			0·230	1·178	−6·21	−5·68	4·89

TABLE 3 — SPIN DENSITIES (ρ_i), ELECTRON DENSITIES (q_i) AND RING PROTON SPLITTING CONSTANTS IN THE RADICAL ANIONS OF SOME AZA-AROMATICS[a] — *contd*

Position[b]	$<S^2>_{ba}$	$<S^2>_{aa}$	ρ_i	q_i	a_i^M	a_i^{CB}	$[a_i]_{obs.}$[c]
			XXXI				
1			0·326	1·039	−8·80	−8·65	7·27
3			−0·009	0·873	0·24	0·27	0·31
4	0·815	0·753	0·128	1·256	−3·46	−3·33	4·19
5			0·120	1·224	−3·24	−2·90	2·48
7			0 001	1·113	−0·03	−0·03	0·31
8			0·277	1·164	−7·48	−6·91	5·49
			XXXII				
1			0·302	1·037	−8·15	−8·00	7·12
3			−0·021	0·877	0·57	0·59	0·10
4	0·818	0·753	0·139	1·246	−3·75	−3·31	2·54
5			0·142	1·176	−3·83	−3·51	4·25
6			0·134	1·141	−3·62	−3·37	4·25
8			0·241	1·201	−6·51	−5·88	5·07
			XXXIII				
1			0·333	1·049	−8·99	−8·79	7·32
3			−0·014	0·866	0·38	0·41	0·29
4	0·821	0·753	0·135	1·261	−3·65	−3·20	4·32
5			0·108	1·196	−2·92	−2·65	2·13
6			0·126	1·091	−3·42	−3·26	4·32
7			−0·026	1·101	0·70	0·68	0·29
			XXXIV				
5	0·796	0·751	0·113	1·128	−3·05	−2·87	2·46
6			0·028	1·092	−0·76	−0·73	1·38
			XXXV				
2	0·821	0·753	0·111	0·986	−3·00	−3·01	3·53
4			0·227	1·161	−6·13	−5·65	5·58
			XXXVI				
3			0·035	0·877	−0·95	−0·99	2·38
4			0·082	1·258	−2·21	−1·93	3·08
5	0·810	0·752	0·111	1·272	−3·00	−2·61	4·04
6			0·026	0·870	−0·70	−0·74	1·56
8			0·394	1·063	−10·64	−10·31	7·72

(a) a_i^M is the splitting constant obtained using the McConnell relation. $a_i^M = -27\,\rho_i$ and Colpa-Bolton relation $a_i^{CB} = -27\rho_i - 12{\cdot}8(1-q_i)\rho_i$.
(b) See Fig. 1.
(c) See references 1-6, 8, 35-36.

The overall agreement with the experimental data is satisfactory.

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